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Journal:	*Environmental Science & Technology*
Manuscript ID	es-2019-02739u.R1
Manuscript Type:	Article
Date Submitted by the Author:	10-Jun-2019
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Sunscreens as a new source of metals and nutrients to coastal waters

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ABSTRACT

Studies detailing the environmental impact of sunscreen products on coastal ecosystems are considered a high priority. In the present study we have determined the release rate of dissolved trace metals (Al, Cd, Cu, Co, Mn, Mo, Ni, Pb and Ti) and inorganic nutrients (SiO_2, P-$PO_4^{3-}$and N-NO_3^-) from a commercial sunscreen in seawater, and the role of UV radiation in the mobilization of these compounds. Our results indicate that release rates are higher under UV light conditions for all compounds and trace metals except Pb. We have developed a kinetic model to establish the release pattern and the contribution to marine coastal waters of dissolved trace metals and inorganic nutrients from sunscreen products. We conservatively estimate that sunscreen from bathers is responsible for an increase of dissolved metals and nutrients ranging from 7.53 x 10^{-4} % for Ni up to 19.8 % for Ti. Our results demonstrate that sunscreen products are a significant source of metals and inorganic nutrients to coastal waters. The normally low environmental

concentrations of some elements (e.g. P) and the toxicity of others (e.g. Pb) could be having a serious adverse effect on marine ecology in the Mediterranean Sea. This risk must not be ignored.

Keywords: Sunscreen, ultraviolet light, metals, inorganic nutrients and kinetic modeling.

INTRODUCTION

Tourism plays a very significant role in the development of coastal areas, especially in Mediterranean countries where, tourism, especially "beach & sun" holidays, has been breaking annual records in recent years[1]. However, tourism can lead to unwanted impacts if it is not developed in a sustainable way. The quality of the water, the rich biodiversity and the natural resources in general of the marine and coastal areas are often threatened by the uncontrolled development of tourism that leads to excessive risk. The sustainable use of our oceans and seas, ensured by the sustainable development and growth of the coastal regions, is considered a priority by the European Union[2].

Research-based knowledge of the ecological impact of tourism and recreational activities on the marine ecosystem is very scarce. For example, seasonal trends in tourism can mediate the timing and effects of the eutrophication of effluent from wastewater; much higher loads are caused by periodic and often predictable surges in the number of visitors at specific times of the year (mainly during summer); and the impacts can extend over a wide area and have effects in areas at considerable distance from the main areas where tourists congregate[3].

Amongst the many chemicals and emerging pollutants that enter the sea and cause adverse ecological effects, sunscreens products in particular are attracting attention in the scientific community, as well as generating significant media coverage in the last few years.

Recently, the interest in these commercial products has increased among scientists and the general public. In the area of human health, experts now insistently recommend the correct application of these products as being essential to help prevent skin cancer due to exposure to ultraviolet (UV) sunlight. In the area of the marine environment, concern has emerged in recent years about the potential hazards for marine ecology caused by the chemical UV filters, both organic (e.g. oxybenzone and octinoxate) and inorganic (Ti and Zn nanoparticles), that are incorporated as ingredients in the formulation of sunscreens. These chemicals are released when the product comes into contact with seawater[4]. On this latter topic, the study of the behavior of metal nanoparticles included in sunscreen formulation and released in the sea is considered very important. For example, it has been reported that nanoparticles can co-occur with other chemicals in aquatic environment and increase the toxicity of them on organisms [5].

Although knowledge is improving about the degradation of individual chemical agents in sunscreens, such as organic (e.g. octyl dimethyl-p-aminobenzoate) and inorganic (TiO_2 nanoparticles) UV filters[6, 7], there is a lack of research that describes the potential release and behavior of chemical ingredients from the total sunscreen matrix in marine waters[8]. This is due to the special physical-chemical characteristics of seawater and the complex matrix of the sunscreen products. For example, the high ionic strength of seawater and organic matter content could promote the agglomeration and sedimentation of nanoparticles[5]. In addition to UV filters, commercial sunscreen contains a great variety of other chemical ingredients that make each of these cosmetic products a complex matrix that is difficult to manage both analytically and environmentally. Sunscreens have also been identified as a significant source of inorganic nutrients, mainly PO_4^{3-}, in coastal and marine waters, raising the possibility of algae blooms in oligotrophic waters[8]. Furthermore, these cosmetics can be a source of high-risk substances such

as metals[9], many of which (i.e. Al, Zn, Mg, Fe, Mn, Cu, Cr and Pb) have been detected and quantified in sunscreens[8, 10].

It has been demonstrated that concentrations of some of these compounds from sunscreens released in coastal water (i.e. PO_4^{3-}, NH_4^+, NO_3^- and Ti) vary during the course of a day, and this could be associated with variations in the beachgoers activities and changes in solar radiation[8]. However, reliable knowledge on the role of sunlight on the release in seawater of the main ingredients found in sunscreen products has not yet been addressed. Sunlight is known to be an important factor in the transformation of chemicals in surface waters[11]. This is especially important in the coastal environment, which is considered to be a "hotspot" of photochemical processes that lead to the transformation of dissolved and particulate compounds[11, 12, 13].

During the aging process and because their hydrophobic characteristics, sunscreen forms stable colloidal residues in seawater, including macroscopic aggregates, agglomerates and submicronic fractions[14]. These compounds can be released to the aqueous phase in the form of dissolved chemicals and colloids through various physical-chemical processes. This study evaluates the differences of dissociation of inorganic compounds/elements under UV light and dark exposure, the kinetics behind the mobilization into the seawater phase, and the amount of these released products included in the fraction <0.22 µm. In particular, experiments on the kinetics of release, using commercial sunscreen, have been conducted in the lab, under controlled UV light and temperature conditions, to evaluate the susceptibility of sunscreen to release metals (Al, Cd, Cu, Mn, Mo, Ni, Pb, Co and Ti) and nutrients (Si-SiO_2, P-PO_4^{3-} and N-NO_3^-) into seawater. Kinetic models are proposed to explain the behavior and variability in seawater of the chemicals studied. This model-based approach offers a valuable potential tool to better understand the risks associated with inorganic nutrients and metals released from sunscreens in the marine coastal ecosystem.

MATERIALS AND METHODS

Seawater collection

Surface water was collected in March 2018 from a zodiac in an offshore area of the Mediterranean Sea (Málaga, Spain; 36.48N, 4.51W) using a peristaltic pump and pumped through acid-cleaned Teflon tubing coupled to a C-flex tubing (for the Cole-Parmer peristaltic pump head), filtered through an acid-cleaned polypropylene cartridge filter (0.22 μm; MSI, Calyx®) and placed in a 25 L low-density polyethylene acid-cleaned plastic carboy. Seawater were filtered in order to avoid the influences that the presence of natural organic matter and organisms could introduce in the elements mobility. The collected seawater was transported to the laboratory and kept at 4ºC in dark conditions prior to experiments. Seawater was stored no longer than two weeks. Prior to performing the experiments, subsamples of seawater were collected for analysis of dissolved inorganic nutrients and metals content.

Metals and inorganic nutrients release kinetics experiment

In this study, we examined the effects of ultraviolet light (280-400 nm) on the kinetics of release of nutrients and metals from one of the most recommended and used commercial sunscreen type (i.e. sun protection milk spray application type with a SPF of 50) (e.g. https://www.consumerreports.org/cro/sunscreens.htm). Laboratory experiments were carried under dark and UV light conditions, mimicking the natural night-time and mid-day conditions respectively, of a Mediterranean coastal area during the summer season. The selection of this particular commercial sunscreen tested was based on: the sun protection factor (SPF 50), the presence of nanoparticles of titanium dioxide among the ingredients; and the format of the sunscreen product, i.e. sun protection milk spray, which has been demonstrated to cause higher toxicity to marine organisms[8]. Metals and inorganic nutrients composition of the selected

104 sunscreen were characterized prior experiments. In both kinetics experiments, 0.8 g of sunscreen
105 was added to 400 mL of seawater in quartz glass vessels (0.5 L capacity). Quartz vessels were
106 used to ensure the penetration of UV light into the seawater sample. During selected time periods
107 (between 0 and 24 h exposure), vessels were gently stirred (simulating movement of water by
108 waves) using a magnetic stirrer, at a controlled temperature of 24ºC representative of seawater
109 temperature in the Mediterranean Sea during the summer[15, 16]. Temperature in the experiments was
110 maintained by cooling water circulation (Polyscience AD07R-40 refrigerated circulating bath).
111 The time periods selected were 0 (immediately after the sunscreen was added), 0.25, 0.5, 1, 3, 6,
112 12 and 24 hours.
113 Samples were exposed to UV radiation of 37.25 ± 3.59 W m^{-2} (average ± SE) using a high-pressure
114 UV lamp (OSRAM, ULTRA VITALUX©, 300W), comparable to the UV component of sunlight.
115 This type of lamp has been used in previous studies related to the degradation of chemical
116 compounds[17] and in the study of sun protection factors[18], among others. The UV light intensity
117 during this experimental period was analogous to the mid-day sunlight in the coastal city of
118 Málaga[19] and corresponds to an ultraviolet index between 8 and10 (considered very high and
119 typical of a summer day on the Mediterranean coast) for the same period in the same place. An
120 UV light meter (UVA-UVB PCE-UV34) was used for UV measurements during the experiment.
121 A diagram of the experimental device under UV light conditions is given in Supporting
122 Information (SI) in Figure S1.
123 In both experiments, at the end of each selected time period, the sample was removed from the
124 quartz chamber and filtered through a 0.22 μm pore-size filter for dissolved chemical analyses, as
125 it represents the soluble and bioavalability fraction. However, we are aware that the filtered
126 solution can contains both, dissolved species and particulate matter < 0.22 μm that are released

from the sunscreen after the experimental exposure. From each sample two subsamples were obtained, one for inorganic nutrient analysis (kept at -20 ºC until analysis) and another subsampled for trace metal analysis (acidified to pH 1.5- 2 with HCL 1M) and kept at 4ºC until preconcentration and analysis. Blanks (seawater sample without sunscreen) were obtained for each selected period and under both light conditions.

Analytical Procedure

Sunscreen characterization. Metals (Al, Cd, Cu, Mn, Mo, Ni, Pb, Co and Ti) and total P and Si in sunscreen were analyzed in triplicate by ICP-MS (PerkinElmer ELAN DRC-e) after prior chemical digestion, following the method described by Páscoa[20]

Seawater chemical analysis. The concentrations of inorganic nutrients (Si-SiO_2, P-PO_4^{3-}, N-NO_2^-, N-NO_3^-) in seawater samples were determined by colorimetric techniques[21] using an autoanalyzer (Skalar San++ System). The accuracy of the analysis was established using reference material for nutrients in seawater (KANSO CRM Japan), with recoveries of 102.5%, 108.3%, 96.4% and 103.9% for Si-SiO_2, P-PO_4^{3-}, N-NO_2^- and N-NO_3^-. Concentrations of Al, Mn and Ti, in seawater were determined directly by ICP-MS (PerkinElmer ELAN DRC-e). Samples for the analysis of Cd, Co, Cu, Mo, Ni and Pb content were previously pre-concentrated using a liquid-organic extraction method with APDC/DDDC[22] and analyzed by ICP-MS (PerkinElmer ELAN DRC-e). The accuracy of metal analysis was checked by the following certified coastal water reference materials for trace metals: CASS-4 N RC-CNRC. The recoveries reported were 93%, 98%, 103%, 93%, 93% and 92 % for Cd, Cu, Mn, Mo, Pb and Co respectively. All the sampling and analytical operations were carried out in accordance with clean techniques for trace metals. All chemical analyses were measured in duplicate. The results are expressed as nmol L^{-1}.

Modeling

The data obtained from the laboratory experiments was modeled and the corresponding parameters were calculated by using Aspen Custom Modeler software (Bedford, Massachusetts, USA) which solves rigorous models and simultaneously estimates parameters. Furthermore, Aspen Custom Modeler gives the statistics values that allow to compare the experimental values of concentration with the values from the mathematical model. The correlation coefficient (R^2), relative standard deviation (RSD) and relative and absolute error were used to check the validity of the model. This tool has been successfully used previously by the authors to model release behavior of contaminants from sediments to seawater[23, 24]. The model parameters were adjusted using an NL2SOL algorithm for the least-square minimization of the deviation between the experimental and theoretical data.

RESULTS AND DISCUSSION

Sunscreen composition. The concentrations of the elements studied in the commercial sunscreen selected and the seawater used in this study are given in Table 1. Titanium (1.48×10^7 μg kg^{-1}) and Al (1.67×10^6 μg kg^{-1}) are the two metals with the highest concentration in the sunscreen. Titanium is present in sunscreen as TiO_2 and TiO_2-nanoparticles, both used as UV filter. The sunscreen contains Al in the form of $Al(OH)_3$, usually used as an opacifying and viscosity-controlling agent[25] and, in some sunscreens, to reduce the agglomeration of the TiO_2 nanoparticles and their catalytic activity in the sunscreen when it is exposed to UV light, and to prevent harmful effects on skin[26, 27]. Results of the analysis also show the presence of other metals in relevant concentrations, including Pb, Mn, Cu, Mo, Ni, Cd, and Co (ranging from 743 μg kg^{-1} for Pb, to 6.10 μg kg^{-1} for Co); these other metals are not described in the sunscreen formulation provided

for users. Metals can be incorporated in cosmetics intentionally because of their function[28] or indirectly, as result of the breakdown of ingredients that incorporate them[29] or due to inadequate purification of raw materials that contain metal impurities[30]. Cobalt may be included as ingredient in the composition of the sunscreen, coating the surface of titanium dioxide nanoparticles powders, to improve their properties performance, as colorant and/or as skin conditioning[31]. In previous studies, concentrations of Al, Cu, Mn, Pb, and Ti in sunscreen products have been reported in a wide range of concentrations (2.20×10^4- 7.40×10^4 μg kg^{-1} for Al; < 900-5.30×10^5 μg Kg^{-1} for Cu; < 200-5.90×10^5 μg Kg^{-1} for Mn; 27.0-1.75×10^3 μg Kg^{-1} for Pb; and 60.0-18.5×10^6 μg Kg^{-1} for Ti)[9, 10].

Table 1. Trace element concentrations in the commercial sunscreen tested and in the seawater (dissolved, <0.22 μm) used in the release kinetics experiments.

Element	Sunscreen content (μg kg^{-1})	Seawater content (nmol L^{-1})
Al	1.67×10^6	235
Cd	16.7	0.0552
Co	6.10	0.0693
Cu	170	1.14
Mn	254	5.27
Mo	137	92.6
Ni	47.5	2.43
Pb	743	0.0703
Ti	1.48×10^7	33.5
P-PO_4^{3-}	3.15×10^5	73.5
Si-SiO_2	3.83×10^6	894
N-NO_3^-	n.a	81.8

Element concentrations in sunscreen are expressed as μg kg^{-1}. Metal and inorganic nutrient concentrations in seawater are expressed as nmol L^{-1}. Phosphorus and silicon were measured as total P and Si form in the sunscreen matrix. n.m means not measured.

Significant concentrations of phosphorous, P (3.15 x 10^5 μg kg^{-1}), and silicon, (3.83 x 10^6 μg kg^{-1}), were also measured in the sunscreen matrix. These nutrients are commonly used in the formulations of these cosmetics. Phosphorus is found in the form of pentasodium ethylenediamine tetramethylene phosphonate, used as a chelating and controlling viscosity agent[32]. Silica, in small concentrations, is also used in these cosmetics for coating TiO_2 nanoparticles[26] and to improve viscosity[33]. Although we were not able to measure the amount of nitrogen compounds in sunscreen, N is present, in amounts depending on the product, in the form of the following nitrogenated compounds: bis-ethylhexyloxyphenol methoxyphenyl triazine, octocrylene, ethylhexyl triazone and drometrizole trisiloxane, used also as UV filters[34-37] and as chelating and viscosity controlling agents[32].

The concentrations of metals and inorganic nutrients measured in the seawater used for the release kinetics experiment (Table 1) are of the same order of magnitude as in Mediterranean coastal seawater[38].

Trace element release. The experimental results obtained for the release of metals and inorganic nutrients from sunscreen to the seawater compartment are plotted in Figure 1. Our results show a clear release of Al, Cu, Mn, Ti, Si-SiO_2 and P-PO_4^{3-} from sunscreen into seawater. However, the release pattern observed for Cd, Mo, Ni, Co and N-NO_3^- was not clear; the concentrations of N-NO_2^- in treatment samples were below the detection limit (< 0.03 μM).

In general, concentrations of released elements were affected by length of time and exposure to UV light. The highest release concentrations of Al, Cd, Co, Cu, Ti, Si-SiO_2 and P-PO_4^{3-} measured were under UV light exposure. Only Mn, Mo and Ni did not show significant ($p > 0.05$; t-test) differences in release rate between light conditions (Figure 1). Average release rates in the first 24 hours were calculated as (C24h-C0h)/24 [nmol L^{-1} h^{-1}]. Release rates decreased in the order Si-SiO_2> P-PO_4^{-3}> Al> Ti> Mo> Mn> Cu> Co, under UV light and Al> SiO_2=P-PO_4^{-3}> Mo> Mn> Cu >Cd> Pb, under dark conditions. Aluminum, SiO_2 and P-PO_4^{-3} had the highest average release rates in both cases. Under UV light conditions Cd, Pb and N-NO_3^- showed maximum concentration ($t \leq 30$ minutes: 1.79 nmol L^{-1}, 0.180 nmol L^{-1} and 2250 nmol L^{-1}, respectively). After 3 hours of experiment, the concentration declined notably (0.120 nmol L^{-1}, 0.0970 nmol L^{-1} and 163 nmol L^{-1}, respectively), reaching a near-equilibrium condition at the end of the exposure. Only Pb clearly increased the concentration more under dark condition than under UV light exposure, reaching a maximum of 0.290 nmol L^{-1} after 12 h. For these elements (i.e. Cd, Pb and N-NO_3^-) dissolution and desorption are favored in the absence of photoreactions. Although more experiments would be necessary to determine the reason for the decrease in concentration of Pb, it is reasonable to conclude that the mechanism for this is adsorption to some of the organic compounds included in the sunscreen formulation. In the case of N-NO_3^-, its action as an oxidant, mediated by photocatalytic reactions, could explain the considerable decrease seen in its concentration in seawater[39].

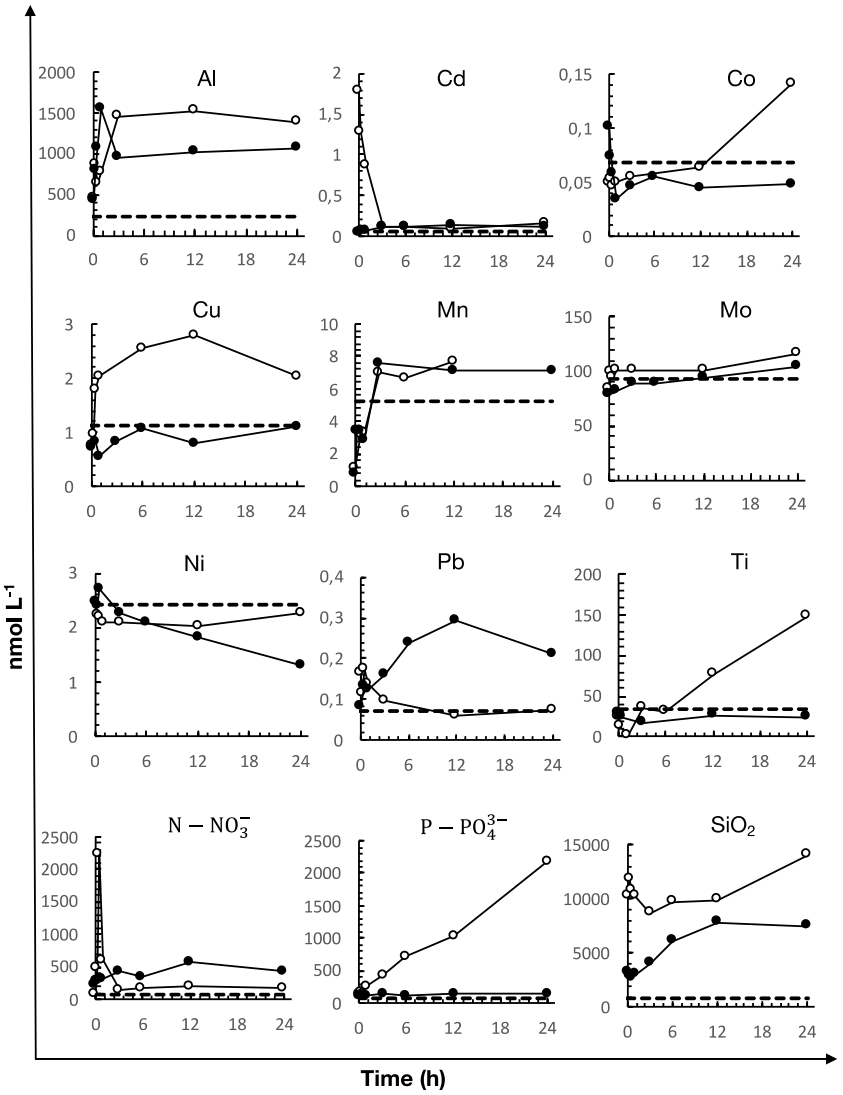


Figure 1. Kinetics of dissolved trace metals and inorganic nutrients released from a commercial sunscreen under UV light (white dots) and under dark conditions (black dots). The horizontal, dashed line depicts the initial concentration of the element in seawater.

Kinetic model of elements release

We have calculated a kinetic model to establish the release pattern and the contribution of trace metals and inorganic nutrients from sunscreen to marine coastal waters. Sunscreen in seawater forms stable colloidal residues that could include macroscopic aggregates, agglomerates and

239 submicronic fractions[14]. The high proportion of organic material in the colloidal residues released
240 from the sunscreen controls the behavior, surface properties and structure of the colloids.
241 Nanoparticles, organic and inorganic chemicals from the sunscreen formulation can interact
242 through several complex processes under different aging times and conditions[5, 40-42]; aggregation
243 rates increase with ionic strength[43]. Figure 2 shows the schematic representation of the chemicals
244 and nanoparticles release proposed in the kinetic scheme (Eq. 4) of aging sunscreen in the seawater
245 environment. The proposed model does not consider the interactions of the studied elements in the
246 air-water and water-sediment interface neither the interactions with natural suspension matter from
247 seawater and organisms. In relation to the nanoparticles, only the behavior of the measured
248 submicronic fraction (<0.22 μm) in seawater is considered. Metals, elements associated with
249 nanoparticles and phosphorous, showed different experimental release behavior and therefore
250 three different kinetic schemes are proposed (Eq. 4). Metals not associated to nanoparticles (Al,
251 Cd, Cu, Mn, Mo, Ni and Pb) are contained mainly inside the organic material; subsequently they
252 are released to the seawater and finally, after an aging period, they can be adsorbed onto the organic
253 material forming a stable colloidal suspension. The elements associated to the nanoparticles (Ti,
254 Co, Si) are initially linked to the organic chemicals due to the hydrophobic character. After a first
255 step, they are unlinked inside the organic material, and later, with a delay of 6h, released to the
256 seawater with an important concentration increasing during the rest of the experiment (6h to 24h);
257 an additional adsorption-desorption stage of these elements can be considered. Phosphorus in
258 sunscreen can be photo-mineralized to inorganic species of $P\text{-}PO_4^{3-}$ [43].
259

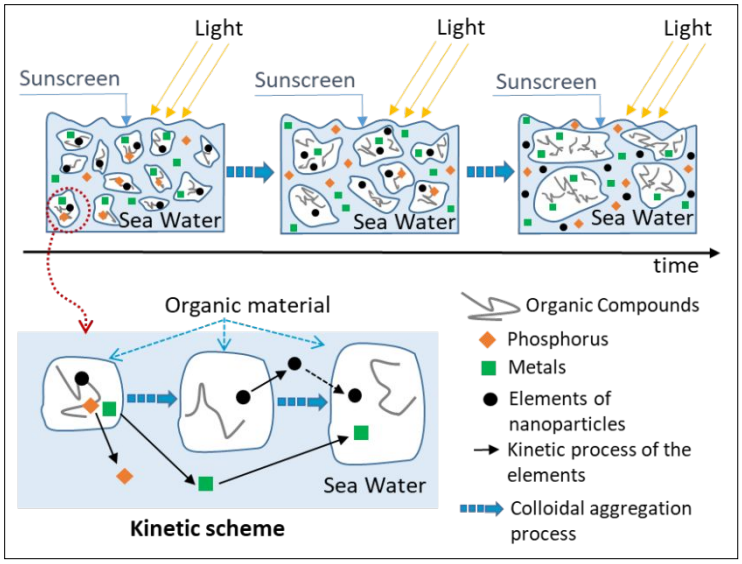


Figure 2. Representation of the dynamic release of the studied chemical elements from sunscreen to seawater under UV light exposure and the aging time, according to the kinetic scheme considered in the eq. 4.

The degradation of organic chemical ingredients of sunscreen has previously been found to follow a pseudo-first-order model[39, 46]. In the present work, the release processes of nutrients and metals from sunscreen in seawater can be modeled considering pseudo-first-order reactions (Eq. 1):

$$r_{i,j} = k_{i,j}[X_i] \quad (1)$$

where $r_{i,j}$ is the reaction rate, $k_{i,j}$ is the rate coefficient of the metal or nutrient i in the reaction j, and $[X_i]$ is the concentration of the reactant i of each reaction. The concentration of metals or nutrients in seawater in each experiment performed at constant volume can be determined by Eq.2:

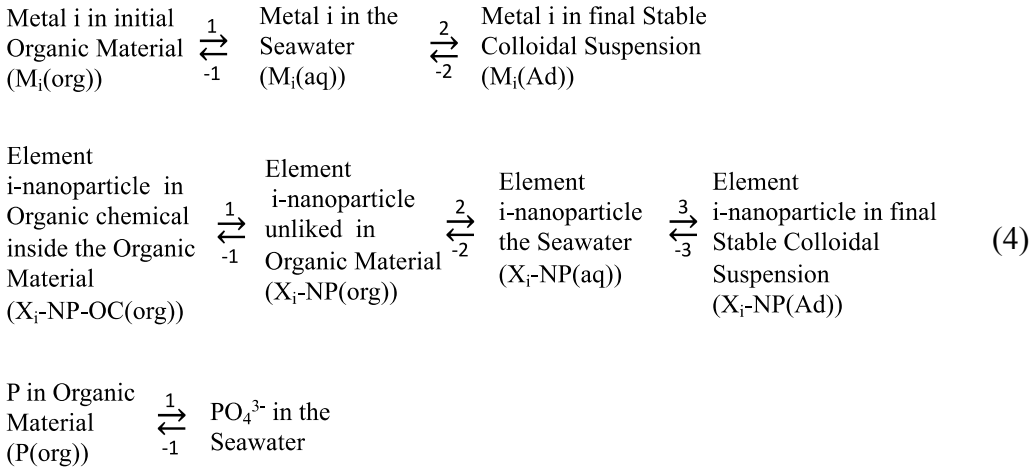
$$\frac{d[X(aq)_i]}{dt} = \sum_{j=1}^{n} r_{i,j} - \sum_{k=1}^{m} r_{i,k} \quad (2)$$

where j is the n reactions that release X (aq) and k the m reactions that adsorb X (aq) from the seawater. The release and adsorption of the components in seawater can take place under total or

equilibrium reaction. In the latter case, the equilibrium constant of component i can be determined by Eq. 3:

$$Ke_{i,j} = \frac{k_{i,j}}{k_{i,-j}} \quad (3)$$

where the subscript j represents the direct reaction of release, and the subscript -j the adsorption. In accordance with the release mechanisms described (Figure 2), three different kinetic schemes (Eq.4) are considered to describe the behavior of metals, elements associated with nanoparticles (Ti, Co and Si), and phosphorus, respectively. In the present work, the liberation of NO_3^- cannot be modeled because of the lack of data on the concentration of total nitrogen and its speciation in sunscreen.



(4)

The values of kinetic constants were estimated considering: the resolution of the mass balances of the eq. 2, the kinetic scheme of the eq. 4, the initial concentration values of elements, and the experimental data of concentration vs. time. The rate coefficients and equilibrium constants of the kinetic reactions estimated, together with the correlation coefficients (R^2) and relative standard deviations (RSD) of the elements released over time, are shown in Table 2. Figure 3 shows the experimental and modeled release of elements over time. The simulated curves adequately fit the experimental results. The release of metals from the sunscreen into seawater can be described by

288 a total reaction for all metals ($Keq_{i,1} = 0$ *in*Table 2), except for Cu in the experiment with UV
289 light, and for Cd in the experiment in darkness. However, their adsorption onto organic material
290 is described by an equilibrium reaction ($Keq_{i,2} \neq 0$) for Cd, Mn, Ni and Pb in the presence of UV
291 light, and for Al, Cd, Cu and Mn in darkness. Elements in the nanoparticles (Ti, Co and Si) are
292 released first to the organic chemicals, later to the seawater and finally adsorbed in the final stable
293 colloidal suspension, except for cobalt for which no adsorption is observed. All reactions of Ti, Co
294 and Si (except for Co without UV light conditions where $Keq_{i,2} \neq 0$), can be described by total
295 reactions ($Keq_{i,j} = 0$ in Table 2). The proposed model predicts reasonably well the observed delay
296 in the mobility of Ti, Co and Si after short exposure times (Figure 3). The $k_{i,1}$ and $k_{i,2}$ kinetic
297 constants obtained for Ti, Co and Si-SiO_2 (Table 2) were equal to each element. This pattern was
298 different from the rest of the studied elements and confirmed the similar origin of these three
299 elements in the system. The release of phosphorous compounds from the organic material to the
300 seawater can be described by a first order reaction.

301
302 **Table 2.** Estimated kinetic rate coefficients $k_{i,j}$ and equilibrium constants $Keq_{i,j}$ for each
303 contaminant in all the assays. The correlation coefficients (R^2) and relative standard deviation
304 (RSD) parameters for the relation between the experimental and simulated released concentrations
305 using the proposed model are also shown.

306

Metals:		Al	Cd	Cu	Mn	Mo	Ni	Pb
Parameter		$M_i(org) \underset{-1}{\overset{1}{\rightleftarrows}} M_i(ac) \underset{-2}{\overset{2}{\rightleftarrows}} M_i(ad)$						
with UV light	$k_{i,1}$ (h^{-1})	0.00647	0.989	0.465	0.310	2.47	0.00671	9.87 x 10^{-4}
	$Keq_{i,1}$	---	---	0.937	---	---	---	---
	$k_{i,2}$ (h^{-1})	0.508	1.07	0.0283	1.31	---	0.444	0.263
	$Keq_{i,2}$	---	19.0	---	0.567	---	0.226	5.44
	RSD	0.183	0.164	0.148	0.132	0.563	0.023	0.208
	R^2	0.911	0.984	0.932	0.964	0.610	0.890	0.788

without UV light	$k_{i,1}$ (h^{-1})	0.0332	0.201	0.0365	0.443	0.337	5.22 x 10^{-5}	0.00960
	$Keq_{i,1}$	---	0.622	---	---	---	---	---
	$k_{i,2}$ (h^{-1})	3.45	0.0501	0.215	0.102	0.0232	0.0263	0.246
	$Keq_{i,2}$	158	0.131	4.02	0.625	---	---	---
	RSD	0.228	0.0548	0.220	0.253	0.779	0.0512	0.168
	R^2	0.701	0.989	0.497	0.876	0.742	0.945	0.888

Element-nanoparticle:		Ti	Co	Si
Parameter		$X_i - NP - OC(org) \underset{-1}{\overset{1}{\rightleftarrows}} X_i - NP(org) \underset{-2}{\overset{2}{\rightleftarrows}} X_i - NP(aq) \underset{-3}{\overset{3}{\rightleftarrows}} X_i - NP(Ad)$		
with UV light	$k_{i,1}$ (h^{-1})	0.00650	0.0518	0.0132
	$Keq_{i,1}$	---	---	---
	$k_{i,2}$ (h^{-1})	0.00641	0.0513	0.0134
	$Keq_{i,2}$	---	---	---
	$k_{i,3}$ (h^{-1})	3.70	---	0.0310
	$Keq_{i,3}$	---	---	---
	RSD	0.171	0.120	0.0599
	R^2	0.975	0.944	0.789
without UV light	$k_{i,1}$ (h^{-1})	1.84 x 10^{-5}	0.731	0.493
	$Keq_{i,1}$	---	---	---
	$k_{i,2}$ (h^{-1})	0.453	0.342	0.00897
	$Keq_{i,2}$	---	0.22	---
	$k_{i,3}$ (h^{-1})	0.465	---	0.287
	$Keq_{i,3}$	---	---	---
	RSD	0.0394	0.093	0.0200
	R^2	0.928	0.956	0.997

Phosphorus:		PO_4^{-3}
Parameter		$P(org) \underset{-1}{\overset{1}{\rightleftarrows}} PO_4^{3-}(ac)$
with UV light	$k_{i,1}$ (h^{-1})	1.71
	$Keq_{i,1}$	---
	RSD	0.0895
	R^2	0.993
without UV light	$k_{i,1}$ (h^{-1})	8.31 x 10^{-5}
	$Keq_{i,1}$	---
	RSD	0.0805
	R^2	0.603

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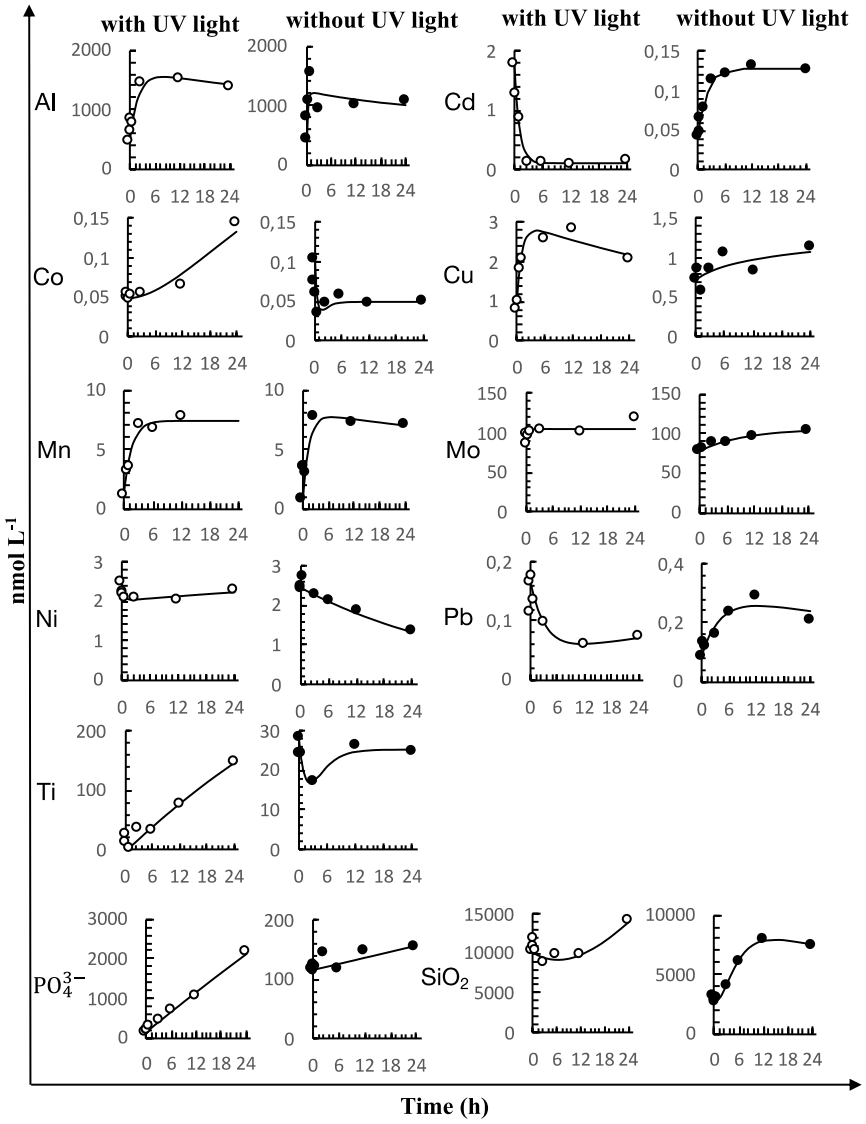

Figure 3. Experimental concentration (mmol L^{-1}) over time of the dissolved metals and nutrients under UV light conditions (white dots), under dark conditions (black dots) and simulated by the proposed model (solid line).

Figure 4 shows the parity plot obtained for the validation of the proposed model in terms of the concentrations of the studied element released, at any time and in both UV light and darkness (n=157). The correlation coefficient (R^2) between the experimental values and the values simulated by the model was 0.979, which indicates a good correspondence between the experimental and

predicted concentrations. A good fit of the proposed model is also confirmed by the fact that 92% of the experimental data lie within a model relative error of ±20%, although larger deviations were noticed at concentrations lower than 0.4 nmol L^{-1}.

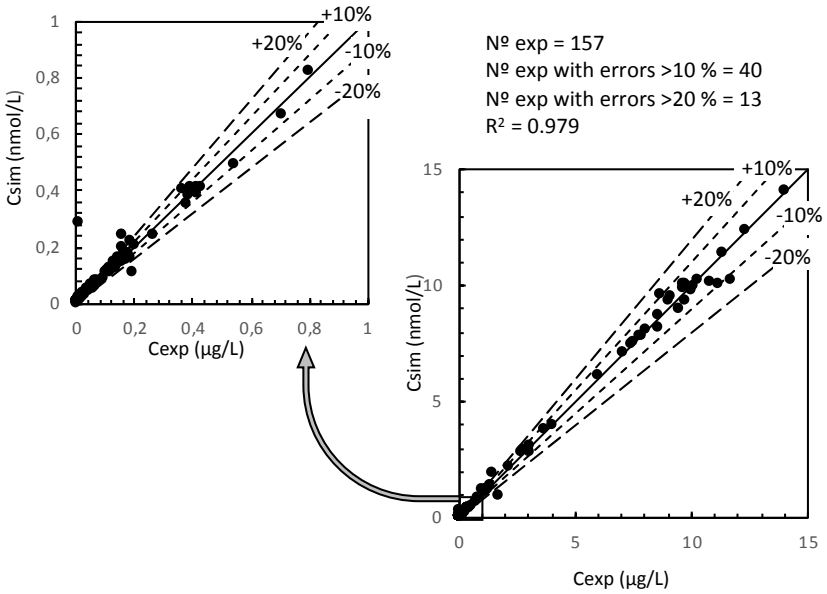

Figure 4. Parity plots of the seawater concentrations from the experimental (Cexp) and simulated (Csim) results of the elements under study. The data number (N) and percentage variation-explained value (R2) are also shown.

The good fit obtained confirms that the proposed model predicts reasonably well the release of contaminants from sunscreen to seawater; an estimation of the maximum concentrations of each element released after 24 hours, the kinetic rate coefficients and equilibrium rate constants are obtained. The obtained model predicts the release of metals and inorganic nutrients under the studied experimental conditions. This model is an useful tool to predict and assess the risk of sunscreens in the sea.

The environmental impact and the consequent potential negative effects of sunscreens ingredients in coastal waters is considered a research priority[2, 4]. Several studies have demonstrated the

numerous effects that individual ingredients have on marine organisms, including the rapid bioaccumulation of UV filters in bivalves, bleaching of corals, and a severe decrease in the recruitment and survival in sea urchin, and others[7, 47-50]. However, identifying sunscreens as a source of releasing metals and nutrients in the marine system and the potential impact of input, has not yet been addressed.

Using the kinetic constants calculated from our experiment results, we have plotted in Figure 5 the estimated increase of concentration of metals and inorganic nutrients derived from the beachgoers during bath in a typical Mediterranean beach on a summer day. To obtain these values, we have made the following assumptions: 1) that one beachgoer uses 1 mg/cm^2 of sunscreen per application, i.e. half of the internationally-recommended amount of sunscreen for a single application[51], about 18 g of sunscreen per person; 2) that at least 25% of the amount of sunscreen applied is washed off during each instance of sea-bathing[52, 53]; 3) the mass flow of sunscreen per hour added to the sea water (kg sunscreen h^{-1}) is determined according to the number of bathers and baths and 4) total volume of sea water of 2.58×10^{-4} m^3, off a typical Mediterranean beach[8]. The parameters used for this simulation are given in SI in Tables S1 and S2. Simulated increase in the concentration (nmol L^{-1} and %) of metals and inorganic nutrients released in a summer day compared to their background levels in seawater (Table 1) is shown in nmol L^{-1} as well as in percentage in SI in Table S3.

The increase of dissolved metals released by the tested sunscreen in seawater could range between 7.5×10^{-4} % for Ni and 20 % for Ti. Titanium, Al, and Pb are the metals that present the most increase in their concentrations, at 20 %, 4 % and 0.2 %, respectively. Several trace metals, at low concentrations (e.g. Co, Mn, Ni, and Cu), play a key biological role in the sea, regulating the biogeochemical function in marine organisms, while others, such as Pb and Cd, could negatively

affect the ecosystem[54, 55]. Thus, small increments of the dissolved concentrations of these metals could have an effect on the marine biota. For example, it has been demonstrated that the induction of phytoplankton cell death in the Mediterranean Sea population is already detectable at concentrations, of both Cd and Pb, of 89 - 96 pmol L^{-1} [56]. Therefore, the release of metals from sunscreen of the order calculated in this study for a typical beach in the Mediterranean Sea, could be having a toxic effect on phytoplankton growth. Although the toxicity of Al to marine biota has hardly been investigated, studies have detected the very high sensitivity of the diatom *Ceratoneis closterium* to this metal (72-h IC_{10} at 593 nmol L^{-1} of Al)[57]. For this metal, a cumulative increase of 4% in Al levels in seawater for a few days could be having a largely unknown effect that surely requires further research. A quantifiable oxidative stress response in the mussel *Mytillus galloprovincialis* has been observed after 24 h of exposure to Ti at 58.5 nmol L^{-1} (corresponding to 0.2 g L^{-1} of sunscreen) under laboratory conditions[49]. The predicted final Ti concentration calculated in our study in seawater (45 nmol L^{-1}) after a summer day, is close to that level, and therefore is another good reason for the potential effect of Ti on the marine environment to be determined.

With respect to the inorganic nutrients in sea water, sunscreen may increase the concentrations of dissolved P-PO_4^{3-} and Si-SiO_2 by 0.2 %, and 0.6% respectively (Figure 5). Although, nitrogen is usually the main limiting nutrient for primary productivity in marine waters[58], in the Mediterranean Sea the main limiting nutrient of primary productivity is P-PO_4^{3-} [59-61]. The low availability of phosphorous in the Mediterranean Sea prevents high primary productivity, leading to oligotrophic conditions. The beaches of this Sea are enjoyed by many millions of visitors every year; the Mediterranean received more than 330 million tourists in 2016, making it the largest tourism

destination in the world[2]. Therefore, a significant supplement of $P\text{-}PO_4^{3-}$ from sunscreen use could be having an important and unpredictable ecological effect in the Mediterranean Sea.

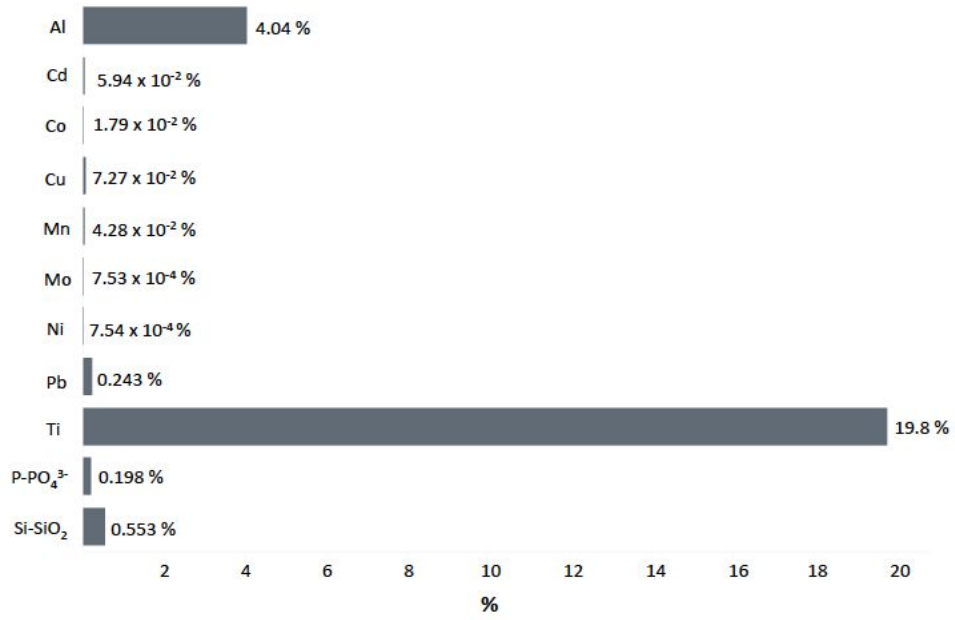

Figure 5. Increase (%) of dissolved metals and inorganic nutrients released from sunscreen after a summer day at a typical Mediterranean beach.

We have used a conservative rate of water renewal of 24 h, but longer water residence times of between 3 -15 days have been recorded for some Mediterranean beaches[62]. In the context of these calculations, water renewal is an essential factor that cannot be ignored due to the associated cumulative effect which could increase the percentages of increase of metals and inorganic nutrients in seawater estimated over time.

Our study confirms that sunscreen is a potential source of dissolved trace metals and inorganic nutrients in coastal waters. Some dissolved element concentrations do not seem to present large differences in release rates between day and night (i.e. Al, Mo, Ni), whereas others show high release rates in daylight (i.e. Co, Cu, $P\text{-}PO_4^{3-}$ and Ti) or in darkness (i.e. Pb) (Figure 1). Our findings suggest that the mobilization of trace metal and inorganic nutrients from sunscreen to

396 seawater could be significantly facilitated by the incidence of UV light. UV radiation can penetrate
397 to depths of least 30 meters in coastal areas, and produces about 50% of total photochemical effects
398 in the marine environment[63]. These effects can change the toxicity of chemicals[64] and could enable
399 greater bio-availability of those trace metals included in sunscreen, thus causing their
400 bioaccumulation in marine organisms. Furthermore, chemicals contained in sunscreen can react
401 under UV radiation and form new compounds, such as hydrogen peroxide[38, 65].
402 The role of UV light in trace elements release from sunscreen is especially important in the context
403 of the assessment of environmental risk presented by these sun protection products[66]. Although
404 the number of studies made to assess the potential effects of sunscreens on marine biota has been
405 increasing recently, the majority of laboratory studies are conducted without UV light at
406 environmentally-relevant conditions, so they are likely to under-estimate the real impacts that
407 sunscreen-related chemicals may have on the natural environment. Therefore, kinetic release
408 studies of sunscreen products under different scenarios of interaction (i.e. diverse types in terms
409 of chemical-physical characteristics) and exposure to UV light (different intensities) are required
410 for a better understanding of the fate of chemicals released from sunscreen in marine waters. It is
411 essential to predict as accurately as possible their potential effects on the vitally-important coastal
412 marine environment.
413
414 ASSOCIATED CONTENT
415 **Supporting Information**
416 Figure S1. Diagram of the experimental device under UV light conditions.
417 Table S1. Parameters and considerations used for simulating of the evolution of metals, Si-SiO_2
418 and P-PO_4^{3-} from tested sunscreen in seawater column.

Table S2. Average number of bathers and flow of sunscreen added to the sea as a function of time, considering the assumptions of table S1.

Table S3. Simulated increase in dissolved metals and inorganic nutrients (nmol L^{-1} and %) on one summer day compared to their background levels of seawater used in this study (Table 1).

This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is funded by the University of Cantabria "Proyecto Puente 2017" (PI: J. Viguri) under the SODERCAN and ERDF Operational Program. The authors thank A. Moreno and D. Roque for their support with field seawater sampling, F. Gómez for his support in constructing the experimental device, A. Silio for lamp characterization and I. Carribero for her assistance with chemical analysis. A. Rodríguez-Romero is supported by the Spanish grant Juan de la Cierva Formación (JCI-2015-26873).

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